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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US97/20735 <b>(22) International Filing Date:</b> 12 November 1997 (12.11.97) <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SAKO, Takashi [JP/JP]; 1-15-7-103, Sumiyoshihonomachi, Higashinada-ku, Kobe 658 (JP). EGOSHI, Yasuhiro [JP/JP]; 9-4-202, Koushien-guchi 6-chome, Nishinomiya, Hyogo 663 (JP). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CONDITIONING SHAMPOO COMPOSITIONS  <b>(57) Abstract</b>  Disclosed is a conditioning shampoo composition comprising by weight: (a) from about 0.05 % to about 50 % of a polyhydrophilic anionic surfactant; (b) from about 0.05 % to about 20 % of a cationic conditioning agent selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof; (c) from about 0.01 % to about 20 % of a silicone compound; and (d) an aqueous carrier.		

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## CONDITIONING SHAMPOO COMPOSITIONS

5

### TECHNICAL FIELD

The present invention relates to conditioning shampoo compositions which  
10 both cleanse the hair and condition the hair.

### BACKGROUND

Human hair becomes soiled due to its contact with the surrounding  
environment and from the sebum secreted by the scalp. The soiling of hair  
15 causes it to have a dirty feel and an unattractive appearance. The soiling of the  
hair necessitates shampooing with frequent regularity.

Shampooing cleans the hair by removing excess soil and sebum.  
However, shampooing can leave the hair in a wet, tangled, and generally  
unmanageable state. Once the hair dries, it is often left in a dry, rough,  
20 lusterless, or frizzy condition due to removal of the hair's natural oils and other  
natural conditioning and moisturizing components. The hair can further be left  
with increased levels of static upon drying, which can interfere with combing and  
result in a condition commonly referred to as "fly-away hair."

A variety of approaches have been developed to alleviate these after-  
shampoo problems. These approaches range from post-shampoo application of  
25 hair conditioners such as leave-on and rinse-off products, to hair conditioning  
shampoos which attempt to both cleanse and condition the hair from a single  
product.

In order to provide hair conditioning benefits in a cleansing shampoo base,  
30 a wide variety of conditioning actives have been proposed. However, many of  
these actives have the disadvantage of leaving the hair feeling soiled or coated,  
of interfering with the cleansing efficacy of the shampoo.

Coacervate formation in a shampoo composition is known to be  
advantageous for providing conditioning benefits to the hair. The use of cationic  
35 polymers to form coacervates are known in the art, such as in PCT publications

WO93/08787 and WO95/01152. However, these shampoo compositions are not capable of delivering satisfactory conditioning benefit while the hair is wet.

Based on the foregoing, there is a need for a conditioning shampoo which can provide improved conditioning benefit when the hair is wet, while not interfering with the cleansing efficacy, nor providing negative feel to the hair when it is dried.

None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY

The present invention is directed to a conditioning shampoo composition comprising by weight: (a) from about 0.05% to about 50% of a polyhydrophilic anionic surfactant; (b) from about 0.05% to about 20% of a cationic conditioning agent selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof; (c) from about 0.01% to about 20% of a silicone compound; and (d) an aqueous carrier.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

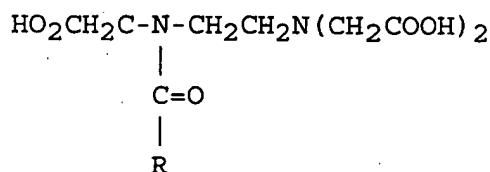
#### POLYHYDROPHILIC ANIONIC SURFACTANT

5       The present invention comprises by weight from about 0.05% to about 50%, preferably from about 0.1% to about 30%, more preferably from about 0.5% to about 20% of a polyhydrophilic anionic surfactant. Polyhydrophilic anionic surfactants useful herein are those having at least two anionic hydrophilic groups in the molecule. One molecule of a polyhydrophilic anionic surfactant may  
10       comprise the same hydrophilic groups, or different hydrophilic groups. Preferably, the hydrophilic group is selected from the group consisting of carboxy, sulfate, sulfonate, and phosphate groups, more preferably at least one carboxy group, still preferably at least two carboxy groups.

Without being bound by theory, it is believed that polyhydrophilic anionic  
15       surfactants herein, with the presence of cationic conditioning agents, are capable of providing a coacervate with a large region which can trap and deliver an increased amount of conditioning agents to the hair surface. It is also believed that coacervates made with polyhydrophilic anionic surfactants herein are readily separated from the water phase, thus also resulting in delivery of an increased  
20       amount of conditioning agents to the hair surface.

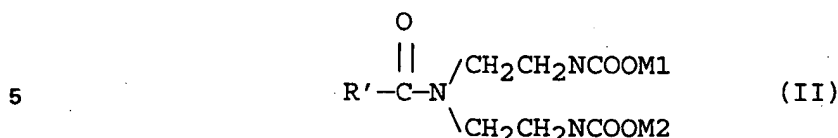
Nonlimiting examples of polyhydrophilic anionic surfactants include N-acyl-L-glutamates such as N-cocoyl-L-glutamate and, N-lauroyl-L-glutamate, sodium lauryl aminodiacetic acid, laurimino dipropionate, and N-lauryl-β-imino-dipropionate, N-acyl-L-aspartate, polyoxyethylene laurylsulfosuccinate, disodium  
25       N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetra sodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; the diamyl ester of sodium sulfosuccinic acid; the dihexyl ester of sodium sulfosuccinic acid; and the dioctyl ester of sodium sulfosuccinic acid, and 2-cocoalkyl N-carboxyethyl N-carboxyethoxyethyl imidazolinium betaine.

30       Other suitable polyhydrophilic anionic surfactants include those of the following formula (I) and (II):



(I)

wherein R is an alkyl of 12 to 18 carbons; and



wherein R' is a straight or branched alkyl or alkenyl of 5 to 21 carbons; and M1 and M2, independently, are hydrogen, alkaline metal, alkaline earth metal, ammonium, alkyl or alkenyl ammonium of 1 to 22 carbons, alkyl or alkenyl substituted pyridinium of 1 to 18 carbons, or basic amino acids. Suitable examples of formula (I) include acid salts of N-acyl-N,N'-ethylenediaminetriacetic acid, such as sodium, triethanolamine and ammonium salts of lauroyl-N,N'-ethylenediaminetriacetic acid, myristoyl-N,N'-ethylenediaminetriacetic acid, cocoyl-N,N'-ethylenediaminetriacetic acid, and oleoyl-N,N'-ethylenediaminetriacetic acid. Suitable examples of formula (II) include acid and salt forms of N-hexanoyl-N-carboxyethyl-β-alanine, N-octanoyl-N-carboxyethyl-β-alanine, N-decanoyl-N-carboxyethyl-β-alanine, N-lauroyl-N-carboxyethyl-β-alanine, N-tetradecanoyl-N-hydroxyethyl-β-alanine, N-hexadecanoyl-N-carboxyethyl-β-alanine, N-isostearyl-N-carboxyethyl-β-alanine, and N-oleoyl-N-carboxyethyl-β-alanine.

Commercially available polyhydrophilic anionic surfactants suitable in the present invention are N-acyl-L-glutamate with a tradename AMISOFT CT-12S, N-cocoyl-L-glutamate with a tradename EMCOL 4400-1 supplied by Witco, lauroyl glutamate with a tradename AMISOFT LS-11, and acylaspartate with tradenames ASPARACK and AAS supplied by Mitsubishi Chemical, sodium lauryl aminodiacetic acid with a tradename NISSAN ANON LA supplied by Nippon Oil and Fat; and N-acyl-N,N'-ethylenediaminetriacetic acid derivatives with tradename ED3A supplied by Hampshire Chemical Corp.

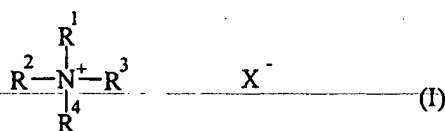
### 30 CATIONIC CONDITIONING AGENT

The present invention comprises by weight from about 0.05% to about 20% of a cationic conditioning agent. The cationic conditioning agents are selected from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof.

### 35 Cationic Surfactant

The cationic surfactants useful herein are any known to the artisan.

Among the cationic surfactants useful herein are those corresponding to the general formula (I):



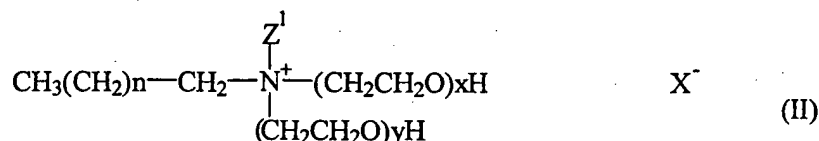
- 5 wherein at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from an aliphatic
- 10 group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals.
- 15 The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from C<sub>1</sub> to about C<sub>22</sub> alkyl. Nonlimiting examples of cationic surfactants useful
- 20 in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

- Among the cationic surfactants of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons.
- 25 Nonlimiting examples of such preferred cationic surfactants include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride,
- 30 dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl

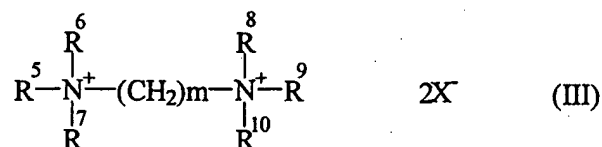


propyleneglycol phosphate dimethyl ammonium chloride, stearyl amidopropyl dimethyl benzyl ammonium chloride, stearyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearyl colamino formyl methy) pyridinium chloride.

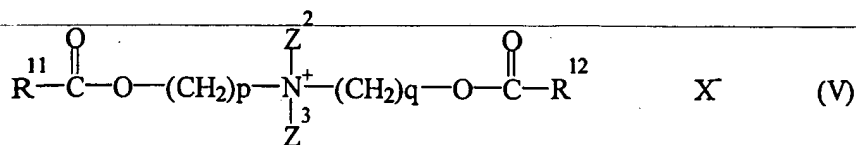
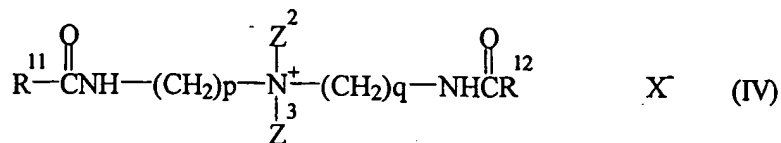
- 5 Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R<sup>1</sup> - R<sup>4</sup> radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C<sub>1</sub> - C<sub>3</sub> alkoxy),  
 10 polyoxyalkylene (preferably C<sub>1</sub> - C<sub>3</sub> polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII)  
 15 below:



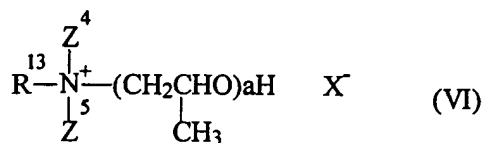
- wherein n is from 8 to about 28, x+y is from 2 to about 40, Z<sup>1</sup> is a short chain alkyl, preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, more preferably methyl, or (CH<sub>2</sub>CH<sub>2</sub>O)<sub>z</sub>H  
 20 wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



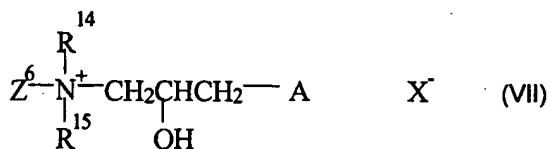
- wherein m is 1 to 5, one or more of R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are independently an C<sub>1</sub> - C<sub>30</sub> alkyl, the remainder are CH<sub>2</sub>CH<sub>2</sub>OH, one or two of R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup> are  
 25 independently an C<sub>1</sub> - C<sub>30</sub> alkyl, and remainder are CH<sub>2</sub>CH<sub>2</sub>OH, and X is a salt forming anion as mentioned above;



- 5 wherein, independently for formulae (IV) and (V),  $\text{Z}^2$  is an alkyl, preferably a  $\text{C}_1$  -  $\text{C}_3$  alkyl, more preferably methyl, and  $\text{Z}^3$  is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl,  $p$  and  $q$  independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2,  $\text{R}^{\text{11}}$  and  $\text{R}^{\text{12}}$ , independently, are substituted or unsubstituted hydrocarbyls, preferably  $\text{C}_{12}$  -  $\text{C}_{20}$  alkyl or alkenyl, and  $\text{X}$  is a salt forming anion as defined above;



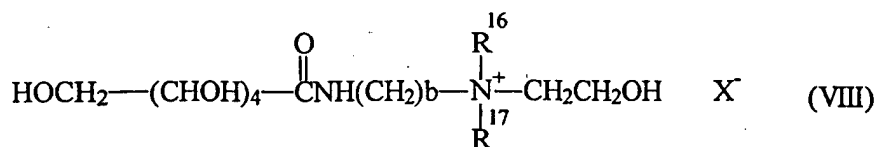
- 15 wherein  $\text{R}^{\text{13}}$  is a hydrocarbyl, preferably a  $\text{C}_1$  -  $\text{C}_3$  alkyl, more preferably methyl,  $\text{Z}^4$  and  $\text{Z}^5$  are, independently, short chain hydrocarbyls, preferably  $\text{C}_2$  -  $\text{C}_4$  alkyl or alkenyl, more preferably ethyl,  $a$  is from 2 to about 40, preferably from about 7 to about 30, and  $\text{X}$  is a salt forming anion as defined above;



20

- wherein  $\text{R}^{\text{14}}$  and  $\text{R}^{\text{15}}$ , independently, are  $\text{C}_1$  -  $\text{C}_3$  alkyl, preferably methyl,  $\text{Z}^6$  is a  $\text{C}_{12}$  -  $\text{C}_{22}$  hydrocarbyl, alkyl carboxy or alkylamido, and  $\text{A}$  is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and  $\text{X}$  is a salt forming anion as defined above;

25



wherein b is 2 or 3, R<sup>16</sup> and R<sup>17</sup>, independently are C<sub>1</sub> - C<sub>3</sub> hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting

5 examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72,

10 quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83,

15 quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethyldimonium salt, and mixtures thereof; for example, commercially available under the following

20 tradenames; VARISOFT 110, VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from

25 Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amido substituted tertiary fatty amines. Such amines,

30 useful herein, include stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine,

palmitamidoethyldimethylamine, behenamidopropyldimethylamine,  
behenamidopropyldiethylamine, behenamidoethyldiethylamine,  
behenamidoethyldimethylamine, arachidamidopropyldimethylamine,  
arachidamidopropyldiethylamine, arachidamidoethyldiethylamine,  
5 arachidamidoethyldimethylamine, diethylaminoethylstearamide. Also useful are  
dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine,  
ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of  
ethylene oxide) stearylamine, dihydroxyethylstearylamine, and  
arachidylbehenylamine. These amines can also be used in combination with  
10 acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic  
acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride,  
and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid.  
Cationic amine surfactants included among those useful in the present invention  
are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981,  
15 which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of  
ammonium quaternary moieties or amino moieties, or a mixture thereof.

#### Cationic Polymers

The hair conditioning compositions of the present invention can further  
20 comprise one or more cationic polymer as a cationic conditioning agent. As used  
herein, the term "polymer" shall include materials whether made by  
polymerization of one type of monomer or made by two (i.e., copolymers) or  
more types of monomers.

Preferably, the cationic polymer is a water-soluble cationic polymer. By  
25 "water soluble" cationic polymer, what is meant is a polymer which is sufficiently  
soluble in water to form a substantially clear solution to the naked eye at a  
concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred  
polymer will be sufficiently soluble to form a substantially clear solution at 0.5%  
concentration, more preferably at 1.0% concentration.

30 The cationic polymers hereof will generally have a weight average  
molecular weight which is at least about 5,000, typically at least about 10,000,  
and is less than about 10 million. Preferably, the molecular weight is from about  
100,000 to about 2 million. The cationic polymers will generally have cationic  
nitrogen-containing moieties such as quaternary ammonium or cationic amino  
35 moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the  
5 Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long  
10 as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair  
15 conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin,  
20 Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and  
25 dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub> - C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub> - C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.  
30

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form,  
35 and then optionally can be converted to ammonium by a quaternization reaction.

Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C<sub>1</sub> - C<sub>7</sub> alkyl, more preferably a C<sub>1</sub> - C<sub>3</sub> alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

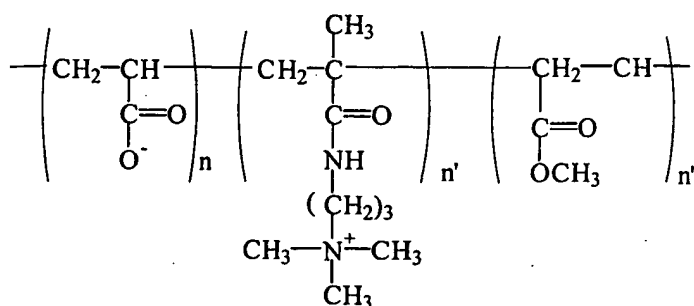
Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub> - C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C<sub>1</sub> - C<sub>7</sub> hydrocarbyls, more preferably C<sub>1</sub> - C<sub>3</sub>, alkyls.

The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral

acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

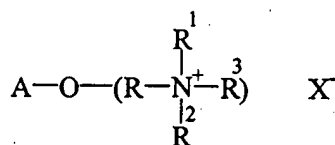
Other suitable cationic polymers are amphoteric terpolymers consisting of acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate, having a structure as shown below referred to in the industry (CTFA) as Polyquaternium 47. An example of a suitable commercial material is MERQUAT 2001® wherein the ratio of n:n':n'' is 45:45:10 supplied by Calgon Corp.



10

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the  
5 polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum  
10 derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated  
15 herein by reference.)

#### SILICONE COMPOUNDS

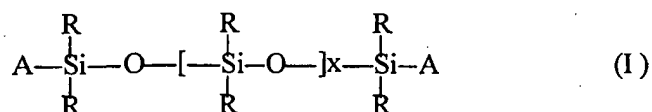
The present invention comprises by weight from about 0.01% to about 20%, preferably from about 0.05% to about 10% of a silicone compound. The silicone compounds useful herein include volatile soluble or insoluble, or  
20 nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The  
25 silicone compounds herein may be made by any suitable method known in the art, including emulsion polymerization. The silicone compounds may further be incorporated in the present composition in the form of an emulsion, wherein the emulsion is made by mechanical mixing, or in the stage of synthesis through emulsion polymerization, with or without the aid of a surfactant selected from  
30 anionic surfactants, nonionic surfactants, cationic surfactants, and mixtures thereof.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 100,000  
35 to about 1,500,000. The viscosity can be measured by means of a glass



capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Silicone compound of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be

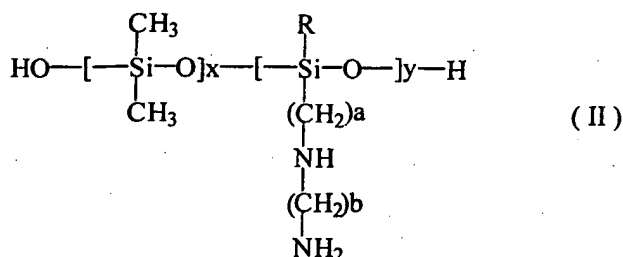
5 mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or

10 mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone compounds include amino substituted materials. Suitable

15 alkylamino substituted silicone compounds include those represented by the following structure (II)



20 wherein R is CH<sub>3</sub> or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

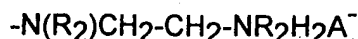
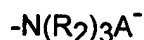
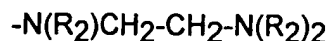
Suitable amino substituted silicone fluids include those represented by the formula (III)



in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number

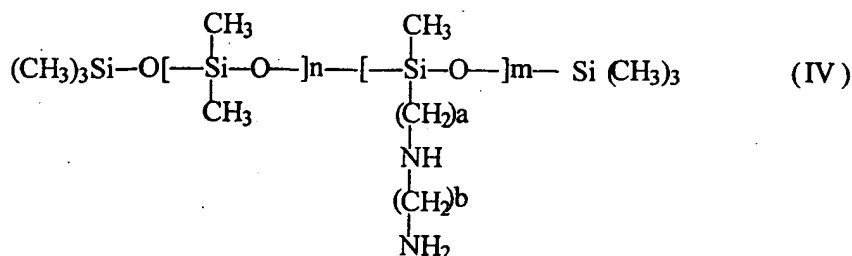
30 from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an

integer from 1 to 2,000 and preferably from 1 to 10;  $R_1$  is a monovalent radical of formula  $C_qH_{2q}L$  in which  $q$  is an integer from 2 to 8 and  $L$  is chosen from the groups



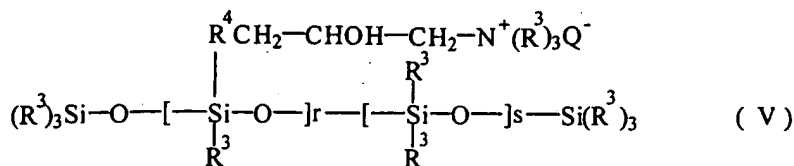
in which  $R_2$  is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and  $A^-$  denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula  $n$  and  $m$  are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



where  $R^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $R^4$  denotes a hydrocarbon radical, preferably a  $C_1 - C_{18}$  alkylene radical or a  $C_1 - C_{18}$ , and more preferably  $C_1 - C_8$ , alkyleneoxy radical;  $Q^-$  is a halide ion, preferably chloride;  $r$  denotes an average statistical value from 2 to 20, preferably from 2 to

8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of

crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl<sup>TM</sup> from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit  $(\text{CH}_3)_3\text{SiO}_{1.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols

indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a  
5 silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl.  
10 Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Commercially available silicone compounds which are highly suitable herein include Dimethicone with tradename D-130, cetyl Dimethicone with tradename DC2502, stearyl Dimethicone with tradename DC2503, emulsified  
15 polydimethyl siloxanes with tradenames DC1664 and DC1784, and alkyl grafted copolymer silicone emulsion with tradename DC2-2845; all available from Dow Corning Corporation, and emulsion polymerized Dimethiconol available from Toshiba Silicone as described in GB application 2,303,857, incorporated herein  
20 by reference.

#### AQUEOUS CARRIER

The compositions of the present invention comprise an aqueous carrier. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

25 The carrier useful in the present invention include water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohol useful herein are monohydric alcohols having 1 to 6 carbons, more preferably ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

30 Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also be used, depending on the desired characteristic of the product. Generally, the compositions of the present invention comprise from about 20% to about 95%, preferably from about 30% to about 92%, and more preferably from  
35 about 50% to about 90% water.

### ADDITIONAL DETERGENT SURFACTANT

The compositions of the present invention may further contain an additional detergent surfactant selected from the group consisting of secondary anionic surfactants, amphoteric surfactants, zwitterionic surfactants, nonionic surfactants, and mixtures thereof. The level and species of the additional detergent surfactant are selected according to the compatibility with other components, and desired characteristic of the product.

In preferred embodiments, the additional detergent surfactant contains a secondary anionic surfactant, more preferably further contains an amphoteric surfactant. In a still preferred embodiment, the additional detergent surfactant is substantially free of alkyl sulfate surfactants.

The term detergent surfactant, as used herein, is intended to distinguish these surfactants from surfactants which are primarily emulsifying surfactants, i.e. surfactants which provide an emulsifying benefit and which have low cleansing performance. It is recognized that most surfactants have both detergent and emulsifying properties. It is not intended to exclude emulsifying surfactants from the present invention, provided the surfactant also possesses sufficient detergent properties to be useful herein.

When present, the additional detergent surfactant is included at a level so that the total of additional detergent surfactant and polyhydrophilic anionic surfactant are from about 5% to about 75%, preferably from about 8% to about 50%, and more preferably from about 10% to about 30%, by weight of the composition.

#### Secondary Anionic Surfactants

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as ammonium, alkanolammonium (e.g., triethanolammonium), a monovalent metal cation (e.g., sodium and potassium), or a polyvalent metal cation (e.g., magnesium and calcium). Preferably, M should be chosen such that the anionic surfactant component is water soluble. The anionic surfactant or surfactants should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the anionic surfactant be soluble in the composition hereof.

Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration, and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, New York, USA), 1988 (ISBN 0-89573-399-0), which is incorporated by reference herein in its entirety.

10 In the alkyl and alkyl ether sulfates described above, preferably R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm oil, tallow, or the  
15 like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are reacted with 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and  
20 neutralized.

Specific examples of alkyl ether sulfates which can be used in the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those  
25 comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% by weight C<sub>12-13</sub> compounds; from about 60% to about 100% by weight of C<sub>14-15-16</sub> compounds, from 0% to  
30 about 20% by weight of C<sub>17-18-19</sub> compounds; from about 3% to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by  
35 weight of compounds having a degree of ethoxylation greater than about 8.



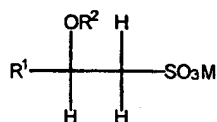
Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula  $[R^1-SO_3-M]$  where  $R^1$  is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C<sub>10-18</sub> n-paraffins.

Other anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $SO_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $SO_2$ , etc., when used in the gaseous form. The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A specific  $\alpha$ -olefin sulfonate mixture of the above type is described more fully in U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967, which is incorporated by reference herein in its entirety.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for

example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278, which are incorporated by reference herein in their entirety.

Another class of anionic surfactants suitable for use in the shampoo compositions are the  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $\text{R}^1$  is a straight chain alkyl group having from about 6 to about 20 carbon atoms,  $\text{R}^2$  is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference in their entirety.

Another class of suitable anionic surfactants are amino acid surfactants which are surfactants that have the basic chemical structure of an amino acid compound, i.e., that contains a structural component of one of the naturally-occurring amino acids.

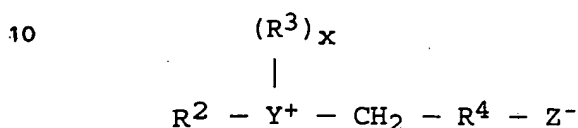
Preferred anionic surfactants for use in the shampoo compositions include ammonium laureth sulfate, triethylamine laureth sulfate, triethanolamine laureth sulfate, monoethanolamine laureth sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium laureth sulfate, potassium laureth sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, N-cocoylalaninate, N-acyl-N-methyl- $\beta$ -alaninate, sodium laurylsarcosinate, cocoyl sarcosine, lauroyl taurate, lauroyl lactylate, N-acyl potassium glycine, lauroamphohydroxy propylsulfonate, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and mixtures thereof.

#### Amphoteric Surfactants

Amphoteric surfactants useful herein include those called zwitterionic surfactants in the art. Amphoteric surfactants useful herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from

about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Amphoteric surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



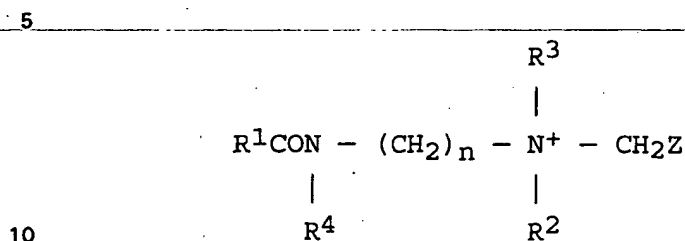
where  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of amphoteric surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidodimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C<sub>8</sub>-C<sub>18</sub> hydrocarbylamidopropylhydroxysultaines, especially C<sub>8</sub>-C<sub>14</sub> hydrocarbylamidopropylhydroxysultaines, e.g., laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula  $RNH(CH_2)_nCOOM$ , the iminodialkanoates of the formula  $RN[(CH_2)_mCOOM]_2$  and mixtures thereof; wherein n and m are numbers from 1

to about 4, R is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Other suitable amphoteric surfactants include those represented by the formula :



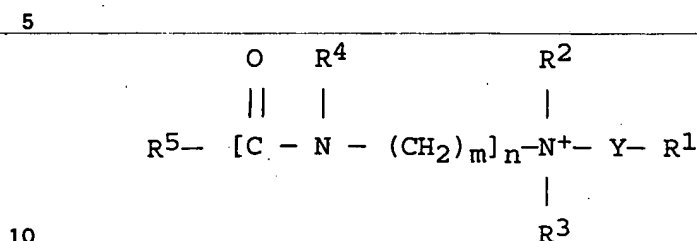
wherein R<sup>1</sup> is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, preferably C<sub>8</sub> - C<sub>16</sub>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of hydrogen, -CH<sub>2</sub>CO<sub>2</sub>M, -CH<sub>2</sub>CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, or -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>H wherein m is an integer from 1 to about 25, and R<sup>4</sup> is hydrogen, -CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R<sup>2</sup>. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38,

MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants, i.e. zwitterionic surfactants, suitable for use in the conditioning compositions are those represented by the formula:



wherein: R<sup>1</sup> is a member selected from the group consisting of

COOM and CH(OH)CH<sub>2</sub>SO<sub>3</sub>M

R<sup>2</sup> is lower alkyl or hydroxyalkyl; R<sup>3</sup> is lower alkyl or hydroxyalkyl; R<sup>4</sup> is a member selected from the group consisting of hydrogen and lower alkyl; R<sup>5</sup> is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl- $\alpha$ -carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-

hydroxypropyl)carboxymethylbetaine, oleyldimethyl- $\gamma$ -carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)- $\alpha$ -carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyldimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful in the conditioning compositions include the amidocarboxybetaines, such as cocamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

#### 15 Nonionic Surfactants

The shampoo compositions of the present invention can comprise a nonionic surfactant. Nonionic surfactants include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Preferred nonlimiting examples of nonionic surfactants for use in the shampoo compositions include the following:

(1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;

(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula [  $R^1R^2R^3N \rightarrow O$  ] where  $R^1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R^2$  and  $R^3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula [  $RR'R''P \rightarrow O$  ] where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which is incorporated herein by reference in its entirety, and which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula  $RO(CH_2CH_2)_nH$  and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula  $R(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$ , wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

#### ANTIDANDRUFF AGENT

The present composition may further comprise a safe and effective amount of an antidandruff agent. When present, the antidandruff agent is

typically used at a level from about 0.1% to about 5%, preferably from about 0.3% to about 5% by weight of the composition.

Without being bound by theory, it is believed that the coacervate made by the polyhydrophilic anionic surfactants and cationic conditioning agents of the present invention are also capable of trapping and effectively delivering the antidandruff agents herein to the hair surface.

Pyrithione salts are useful herein. Suitable pyrithione salts are heavy metal salts of 1-hydroxy-2-pyridinethione, the heavy metal salts being zinc, tin, cadmium, magnesium, aluminium, and zirconium. Preferred is zinc salt of 1-hydroxy-2-pyridinethione known in the art as zinc pyrithione, more preferably in a particle size of up to about 20 microns, still preferably from about 1 to about 10 microns. Commercially available pyrithione salts suitable herein include Zinc Pyrithione available from Olin.

Selenium sulfides are useful herein. Selenium sulfides herein include selenium disulfide, as well as  $Se_xS_y$  in cyclic structure, wherein x and y are integers and  $x + y$  equals 8. Preferred selenium sulfides are those having a particle size of less than about 15 microns, more preferably less than about 10 microns; wherein the particle size is measured by a laser light scattering device such as Malvern 3600 instrument.

Sulfur and octopirox, its salts, and its derivatives are also useful herein.

Antidandruff agents as mentioned above can be used alone, or in combination with one another.

#### ADDITIONAL CONDITIONING AGENTS

The compositions of the present invention may further comprise from about 0.05% to about 20%, preferably from about 0.1% to about 10%, and more preferably from about 0.5% to about 10% of additional conditioning agents selected from the group consisting of high melting point compounds, oily compounds, and nonionic polymers.

#### High Melting Point Compound

The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of



combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as

steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C<sub>1</sub>-C<sub>30</sub> alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

### Oily Compound

The compositions comprise an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds  
5 useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second  
10 oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic  
15 Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

#### First Oily Compound

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols  
20 can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

25 The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic  
30 acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol  
35 derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl

linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, 5 Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylolpropane trioleate, and trimethylolpropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylolpropane triisostearate with 10 tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylolpropane trioleate with a tradename ENUJERUBU available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl 15 isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

#### Second Oily Compound

The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, 20 so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C<sub>2-6</sub> alkenyl monomers. These polymers can 25 be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 30 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, 35 polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are

hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA),  $\alpha$ -olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co., and trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co.

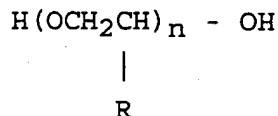
#### Nonionic Polymer

Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

#### Polyalkylene Glycols

These compounds are particularly useful for compositions which are designed to impart a soft, moist feeling to the hair. When present, the polyalkylene glycol is typically used at a level from about 0.025% to about 1.5%, preferably from about 0.05% to about 1%, and more preferably from about 0.1% to about 0.5% of the compositions.

The polyalkylene glycols are characterized by the general formula:



wherein R is selected from the group consisting of H, methyl, and mixtures thereof. When R is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R is methyl, these materials are polymers of propylene oxide, which are  
5 also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, n has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably  
10 from about 3500 to about 15,000.

Polyethylene glycol polymers useful herein are PEG-2M wherein R equals H and n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R equals H and n has an average value of about 5,000 (PEG-5M is  
15 also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R equals H and n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R equals H and n has an average value of about 9,000 (PEG 9-M is also known  
20 as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R equals H and n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

#### 25 ADDITIONAL COMPONENTS

The shampoo compositions of the present invention may include a variety of additional components, which may be selected by the artisan according to the desired characteristics of the final product. Additional component include, for example, polyvalent metal cations, suspending agents, ethoxylated glucose  
30 derivatives, and other additional components.

#### Polyvalent Metal Cations

Suitable polyvalent metal cations include divalent and trivalent metals, divalent metals being preferred. Exemplary metal cations include alkaline earth metals, such as magnesium, calcium, zinc, and copper, and trivalent metals such  
35 as aluminum and iron. Preferred are calcium and magnesium.

The polyvalent metal cation can be added as an inorganic salt, organic salt, or as a hydroxide. The polyvalent metal cation may also be added as a salt with anionic surfactants as mentioned above.

Preferably, the polyvalent metal cation is introduced as an inorganic salt or organic salt. Inorganic salts include chloride, bromide, iodine, nitrate, or sulfate, more preferably chloride or sulfate. Organic salts include L-glutamate, lactate, malate, succinate, acetate, fumarate, L-glutamic acid hydrochloride, and tartarate.

It will be clear to those skilled in the art that, if polyvalent salts of the anionic surfactant is used as the mode of introducing the polyvalent metal cations into the compositions hereof, only a fraction of the anionic surfactant may be of polyvalent form, the remainder of the anionic surfactant being necessarily added in monovalent form.

Hardness of the conditioning shampoo compositions can be measured by standard methods in the art, such as by ethylene diamine tetraacetic acid (EDTA) titration. In the event that the composition contains dyes or other color materials that interfere with the ability of EDTA titration to yield a perceptible color change, hardness should be determined from the composition in the absence of the interfering dye or color.

#### Suspending Agents

A preferred additional component is a suspending agent, particularly for compositions comprising silicone compounds of high viscosity and/or large particle size. When present, the suspending agent is in dispersed form in the compositions. The suspending agent will generally comprise from about 0.1% to about 10%, and more typically from about 0.3% to about 5.0%, by weight, of the composition.

Preferred suspending agents include acyl derivatives such as ethylene glycol stearates, both mono and distearate, long chain amine oxides such as alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide, and mixtures thereof. When used in the shampoo compositions, these preferred suspending agents are present in the composition in crystalline form. These suspending agents are described in U.S. Patent 4,741,855.

Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic

monoethanolamide, cocomonoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate.

Other suitable suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly  
5 N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Other suitable suspending agents include xanthan gum. The use of xanthan gum as a suspending agent in silicone containing shampoo  
10 compositions is described, for example, in U.S. Patent 4,788,006, which is incorporated herein by reference in its entirety. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which is incorporated herein by reference in its entirety.

15 Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which is incorporated herein by reference in its entirety. Examples of these polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with an  
20 allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propylene. Neutralizers may be required, for example, amino methyl propanol, triethanol amine, or sodium hydroxide.

Other suitable suspending agents can be used in the compositions, including those that can impart a gel-like viscosity to the composition, such as  
25 water soluble or colloiddally water soluble polymers like cellulose ethers such as hydroxyethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, and materials such as guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives.

#### Ethoxylated Glucose Derivatives

30 A preferred additional component is an ethoxylated glucose derivative, particularly for increasing the viscosity of compositions, and for the phase stability of compositions at high and low temperatures. When present, the ethoxylated glucose derivative is included at a level of from about 0.1% to about 10%, and more typically from about 0.3% to about 5.0%, by weight, of the  
35 composition.



Suitable ethoxylated glucose derivatives include methyl gluceth 10, methyl gluceth 20, PEG-120 methylglucose dioleate, PPG-10 methylglyucose ether, and PPG-20 methylglyucose ether. Commercially available material highly suitable herein include methyl gluceth 10 with tradename GLUCAM E-10, PEG-120 methylglucose dioleate with tradename Glucamate DOE-120, PPG-10 methylglucose ether with tradename GLUCAM P-10, and PPG-20 methylglucose ether with tradename GLUCAM P-20, all available from Amerchol.

#### Other Additional Components

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolyzed collagen with tradename Peptin 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; emulsifying surfactants for dispersing water insoluble components in the carrier; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; optical brighteners such as polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate. Such optional ingredients generally are used individually at levels from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% by weight of the composition.

#### **EXAMPLES**

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as

limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
N-cocoyl-L-glutamate *1	4	0	0	0	8	18
Disodium Lauryl Sulfosuccinate *2	0	5	0	0	0	0
N-acyl-L- Aspartate *3	0	0	5	0	0	0
Sodium Lauryl Aminodiacetic acid *4	0	0	0	5	0	0
Cocamidopropylbetaine *5	4	5	5	5	0	0
Ammonium Laureth-3 Sulfate	10	10	10	10	10	0
Behenyl trimethylamonium chloride*6	0.5	0.25	0.5	0.5	0.5	0.5
Polyquaterium-10 *8	0.5	0.5	0.5	0.5	1.0	2.0
Silicone Emulsion 1 *11	2.0	0	0	0	0	0
Silicone Emulsion 2 *12	0	0	2.0	0	0	0
Dimethicone *13	0	3.0	0	0	0	0
Silicone Emulsion *14	0	0	0	0	0	2.0
Alkyl Silicone *15	0	0	0	0	2.0	0
Alkyl Silicone Emulsion *16	0	0	0	2.0	0	0
Cetyl Alcohol	0.5	0	0	0	1.0	0
Cocamide MEA	1.5	1.5	1.5	1.5	1.5	3.0
Ethylene Glycol Distearate	1.5	3.0	1.5	1.5	0	6.0
Perfume solution	0.5	0.5	0.5	0.5	0.5	0.5
DMDM Hydantoim	0.37	0.37	0.37	0.37	0.37	0.37
PEG120 Methyl Glucose Dioleate *17	0.5	0	0	1.0	1.5	3.0
MgCl <sub>2</sub>	0.5	0	0	0	0	0
MgSO <sub>4</sub>	0	0.5	0	0	0	0
Deionized Water	-----q.s. to 100%-----					

	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
N-cocoyl-L-glutamate *1	4	10	10	5	10	5
Disodium Lauryl Sulfosuccinate *2	0	5	0	0	0	0
N-acyl-L- Aspartate *3	0	0	5	0	0	0
Sodium Lauryl Aminodiacetic acid *4	0	0	0	5	0	0
Cocamidopropylbetaine *5	4	5	10	5	10	0
Cocoamidohydroxysultaine *18	0	0	0	0	0	5
Ammonium Laureth-3 Sulfate	10	0	0	10	0	10
Behenyl trimethylamonium chloride*6	1.0	0	0.5	0	0.5	0.5
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate *7	0	0	0	1.0	0	0
Polyquaterium-10 *8	0.25	0.5	1.0	0.5	1.0	2.0
Polyquaterium-24 *9	0.25	0	0	0	0	0
Polyquaterium-47 *10	0	0.5	0	0	0	0
Silicone Emulsion 1 *11	2.0	0	0	2.0	0	0
Silicone Emulsion 2 *12	0	0	2.0	0	2.0	0
Dimethicone *13	0	3.0	0	0	0	2.0
Cocamide MEA	1.5	1.5	1.5	3.0	5.0	3.0
Ethylene Glycol Distearate	1.5	3.0	1.5	1.5	0	3.0
Perfume solution	0.5	0.5	0.5	0.5	0.5	0.5
DMDM Hydantoim	0.37	0.37	0.37	0.37	0.37	0.37
PEG120 Methyl Glucose Dioleate *17	0	0	0	0	1.5	0
Methyl Gluceth-20 *18	0.5	0	0	1.0	0	0
MgCl <sub>2</sub>	0.5	0	0	0	0	0
MgSO <sub>4</sub>	0	0	0.5	0	0	0.5
Deionized Water	-----q.s. to 100%-----					

	Ex. 13	Ex. 14	Ex. 15	Ex. 16
N-cocoyl-L-glutamate *1	4	4	10	5
Disodium Lauryl Sulfosuccinate *2	0	0	0	0
N-acyl-L- Aspartate *3	0	0	5	0
Sodium Lauryl Aminodiacetic acid *4	0	0	0	5
Cocamidopropylbetaine *5	4	5	10	5
Cocoamidohydroxysultaine *18	0	0	0	0
Ammonium Laureth-3 Sulfate	10	0	0	10
Behenyl trimethylamonium chloride*6	0.5	0.5	0.5	0
Polyquaterium-10 *8	0.5	0.5	1.0	0.5
Silicone Emulsion 1 *11	2.0	0	2.0	2.0
Dimethicone *13	0	3.0	0	0
Zinc Pyrithion*23	0	0	1.0	1.0
Cocamide MEA	1.5	1.5	1.5	3.0
Ethylene Glycol Distearate	1.5	1.5	1.5	1.5
PEG120 Methyl Glucose Dioleate *17	0	0	0	0.5
Methyl Gluceth-20 *18	0.5	0	0	0
Hydrolyzed Collagen *19	0.01	0	0	0
Vitamine E *20	0	0.01	0	0.01
Panthenol *21	0	0.025	0	0.025
Panthenyl Ethyl Ether *22	0	0.025	0	0.025
Perfume solution	0.5	0.5	0.5	0.5
DMDM Hydantoim	0.37	0.37	0.37	0.37
MgSO <sub>4</sub>	0	0	0.5	0
Deionized Water	-----q.s. to 100%-----			

### Definitions

- \*1 Amisoft CT-12S obtained from Ajinomoto.
- 5 \*2 Emcol 4400-1 obtained from Witco
- \*3 Asparak obtained from Mitsubishi
- \*4 Nissan Anon LA obtained from Nippon Oil and Fat
- \*5 Tego Betaine F obtained from TH Goldschmidt
- \*6 Econol TM22 obtained from Sanyo Kasei
- 10 \*7 Varisoft 110 obtained from Witco

- \*8 UCare Polymer LR400 obtained from Amerchol
- \*9 Quatrisoft Polymer LM-200 obtained from Amerchol
- \*10 Merquat 2001 obtained from Calgon
- \*11 Emulsion of 1,00,000cp Dimethiconol with particle size of approximately  
5 200nm obtained from Toshiba Silicone

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- \*12 Emulsion of 500,000cp Dimethiconol with particle size of approximately  
200nm obtained from Toshiba Silicone
- \*13 40(gum)/60(fluid) weight ratio blend of SE-76 dimethicone gum obtained  
from General Electric Silicone
- 10 \*14 Emulsion of 60,000csk polydimethyl siloxane with particle size of  
approximately 300nm obtained as DC1664 from Dow Corning
- \*15 Silicone alkyl grafted copolymer DC2502 obtained from Dow Corning
- \*16 Alkyl grafted copolymer silicone emulsion DC2-2845 from Dow Corning
- \*17 GLUCAMATE DOE-120 obtained from Amerchol
- 15 \*18 GLUCAM E-20 obtained from Amerchol
- \*19 Peptin 2000 obtained from Hormel
- \*20 Emix-d obtained from Eisai
- \*21 available from Roche
- \*22 available from Roche
- 20 \*23 available from Olin

#### Method of Preparation

The shampoo compositions of Examples 1 through 16 as shown above  
can be prepared by any conventional method well known in the art. Suitable  
25 methods are described below.

Polymers and surfactants are dispersed in water to form a homogenous  
mixture. To this mixture are added the other ingredients except for silicone  
emulsion (if present), perfume, and salt; the obtained mixture is agitated. If a  
silicone blend is present, the silicone emulsion is made with the silicone blend, a  
30 small amount of deterative surfactant, and a portion of water. The obtained  
mixture is then passed through a heat exchanger to cool, and the silicone  
emulsion, perfume, and salt are added. The obtained compositions are poured  
into bottles to make hair shampoo compositions. Alternatively, water and  
surfactants and any other solids that need to be melted can be mixed together at  
35 elevated temperature, e.g., above about 70°C, to speed the mixing into

shampoo. Additional ingredients can be added either to this hot premix or after cooling the premix. The ingredients are mixed thoroughly at the elevated temperature and then pumped through a high shear mill and then through a heat exchanger to cool them to ambient temperature. If present in the composition, 5 silicone emulsified at room temperature in concentrated surfactant is added to  
the cooled mix.

Examples 1 through 16 have many advantages. For example, improved squeaky hair feel, softness, smoothness and combing ease during rinsing and after rinsing as well as overall dry conditioning benefits.

10 It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

## WHAT IS CLAIMED IS:

1. A conditioning shampoo composition comprising by weight:
  - (a) from about 0.05% to about 50% of a polyhydrophilic anionic surfactant;
  - (b) from about 0.05% to about 20% of a cationic conditioning agent selected  
5 from the group consisting of cationic surfactants, cationic polymers, and mixtures thereof;
  - (c) from about 0.01% to about 20% of a silicone compound; and
  - (d) an aqueous carrier.
2. The conditioning shampoo composition according to Claim 1 wherein the polyhydrophilic anionic surfactant comprises at least one carboxy group in the molecule.
3. The conditioning shampoo composition according to Claim 1 further comprising an additional deterative surfactant.
4. The conditioning shampoo composition according to Claim 3 wherein the additional deterative surfactant comprises a secondary anionic surfactant and an amphoteric surfactant, wherein the total of the polyhydrophilic anionic surfactant and the additional deterative surfactant are from about 5% to about 75% by  
5 weight of the composition.
5. The conditioning shampoo composition according to Claim 4 wherein the composition is substantially free of alkyl sulfate surfactants.
6. The conditioning shampoo composition according to Claim 1 wherein the cationic surfactant contains in the molecule at least one alkyl chain having at least 16 carbons.
7. The conditioning shampoo composition according to Claim 1 wherein the cationic polymer is selected from Polyquaternium 10, Polyquaternium 24, and mixtures thereof.

8. The conditioning shampoo composition according to Claim 1 wherein the silicone compound is a dimethicone having a viscosity of from about 100,000 centistokes to about 1,500,000 centistokes.

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9. The conditioning shampoo composition according to Claim 1 wherein the silicone compound is an emulsion polymerized silicone polymer wherein the silicone polymer is dispersed as a particle having an average size of not more than about 450 nm.

10. The conditioning shampoo composition according to Claim 9 wherein the emulsion polymerized silicone polymer is selected from the group consisting of a dimethiconol having a molecular weight of at least 100,000, an amodimethicone having a molecular weight of at least 10,000, and mixtures thereof.

11. The conditioning shampoo composition according to Claim 10 wherein the silicone emulsion comprises the silicone polymer dispersed as a particle having an average size of from about 150nm to about 250nm.

12. The conditioning shampoo composition according to Claim 1 further comprising by weight from about 0.1% to about 5% of an antidandruff agent.

13. The conditioning shampoo composition according to any of the preceding claims further comprising by weight from about 0.05% to about 20% of an additional conditioning agent selected from the group consisting of high melting point compounds, oily compounds, nonionic polymers, and mixtures thereof.



# INTERNATIONAL SEARCH REPORT

National Application No  
PCT/US 97/20735

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/06 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 32919 A (THE PROCTER AND GAMBLE CO.) 24 October 1996 see page 8, line 21-34; claim 1; examples ---	1-8,10
X	WO 95 01152 A (THE PROCTER AND GAMBLE CO.) 12 January 1995 cited in the application see page 29, line 35 - page 30, line 3 see page 19, line 24-40; claims 1,4-8 ---	1-8,10
X	US 5 217 652 A (IOVANNI, C. F.) 8 June 1993 see claims 1,3 ---	1
X	WO 97 26860 A (JOHNSON & JOHNSON) 31 July 1997 see claims 1,10,12,15,20,24,27 ---	1-8
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Beyss, E

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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